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(54) HYDROGEN STORAGE ALLOY ELECTRODE FOR ALKALINE STORAGE BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To suppress the generation of an oxygen gas on a hydrogen storage alloy electrode even if over discharge is conducted by containing calcium carbonate in the active material layer of the electrode containing hydrogen storage alloy and having the active material.

SOLUTION: Calcium carbonate is contained in an active material layer. When the calcium carbonate is added, the oxygen generating potential of a hydrogen storage alloy electrode becomes a nobler potential. When the calcium carbonate is contained in the active material layer, the generation of an oxygen gas on the hydrogen storage alloy electrode can be suppressed even if over discharge is conducted. As the result, the oxidization of the hydrogen storage alloy can be suppressed so that the deterioration of hydrogen storage characteristics can be suppressed. Preferably, the containing amount of the calcium carbonate is 0.1 to 3.0 percentage by weight against the hydrogen storage alloy. When the containing amount of the calcium carbonate becomes 0.1 percentage by weight or more, the rate of discharge capacity after the over discharge to the discharge capacity before the over discharge becomes high. When the same exceeds 3.0 percentage by weight, the temperature characteristics of a battery at a low temperature are deteriorated, and battery characteristics are deteriorated.

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CLAIMS

[Claim(s)]
[Claim 1]An alkaline battery service-water matter occlusion alloy electrode, wherein calcium carbonate contains in said active material layer in an alkaline battery service-water matter occlusion alloy electrode which has an active material layer containing a hydrogen storing metal alloy.
[Claim 2]The alkaline battery service-water matter occlusion alloy electrode according to claim 1, wherein content of said calcium carbonate is 0.1 to 3.0 % of the weight to said hydrogen storing metal alloy.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to an alkaline battery service-water matter occlusion alloy electrode.
[0002]
[Description of the Prior Art]Since alkaline batteries, such as a nickel hydrogen storage battery using a hydrogen storing metal alloy electrode as a negative electrode, have a high energy density and there is little environmental pollution, they attract attention especially in recent years. Generally a hydrogen storing metal alloy electrode is manufactured as follows. First, what carried out the heating and dissolving of what added various kinds of metal to Mm (mesh metal), a Ni alloy, etc. which used the lantern as the main ingredients is ground, and hydrogen storing metal alloy powder is made. Next, this hydrogen storing metal alloy powder and binder are kneaded, a paste is made, and charge collectors, such as a punching metal, are filled up with this paste. And this is dried, and it presses and completes. When a cell charges, occlusion of the hydrogen is carried out to a hydrogen storing metal alloy.
[0003]
[Problem(s) to be Solved by the Invention]However, when the usual charge and discharge were performed after carrying out overdischarge of the alkaline battery using a hydrogen storing metal alloy electrode as a negative electrode, it had the problem that the service capacity before performing overdischarge could not be obtained. the nickel hydrogen storage battery combined with the anode which used nickel hydroxide as the main ingredients -- about -- if overdischarge is carried out to -1.0V, the service capacity before performing overdischarge cannot be obtained. This is because an anode and a negative electrode will carry out a polarity inversion and oxygen gas will be emitted from a hydrogen storing metal alloy electrode, if overdischarge is carried out to abbreviation-1.0V. Thus, generating of oxygen gas will oxidize and degrade a hydrogen storing metal alloy. The hydrogen absorption characteristic of a hydrogen storing metal alloy falls, and service capacity stops as a result, recovering (the service capacity before performing overdischarge cannot be obtained). Thus, especially in the hydrogen storing metal alloy electrode, recovery of the service capacity after overdischarge

was difficult.

[0004]Even if the purpose of this invention performs overdischarge, there is in providing the alkaline battery service-water matter occlusion alloy electrode which controls generating of the oxygen gas on a hydrogen storing metal alloy electrode, and can recover service capacity.

[0005]

[Means for Solving the Problem]This invention makes an active material layer contain calcium carbonate ($CaCO_3$) for an alkaline battery service-water matter occlusion alloy electrode which has an active material layer containing a hydrogen storing metal alloy. If calcium carbonate is made to add, as for a hydrogen storing metal alloy electrode, oxygen evolution potential will turn into electropositive potential more. Then, like this invention, if an active material layer is made to contain calcium carbonate, even if it performs overdischarge, generating of oxygen gas can be controlled. As a result, oxidation of a hydrogen storing metal alloy can be controlled and a fall of the hydrogen absorption characteristic of a hydrogen storing metal alloy can be controlled. Calcium carbonate is stable also in an alkali solution.

[0006]As for content of calcium carbonate, it is preferred to consider it as 0.1 to 3.0 % of the weight to a hydrogen storing metal alloy. If content of calcium carbonate will be 0.1% of the weight or more to a hydrogen storing metal alloy, a rate (recovery capacity rate) of service capacity after overdischarge to service capacity before overdischarge will become high. If content of calcium carbonate exceeds 3.0 % of the weight to hydrogen storing metal alloy powder, temperature characteristics (service capacity ratio of low temperature/ordinary temperature) in low temperature of a cell will fall, and a battery characteristic will fall.

[0007]

[Embodiment of the Invention]Each alkaline battery service-water matter occlusion alloy electrode used for the examination was manufactured as follows. First, this was cooled after carrying out the heating and dissolving of what added Co of the specified quantity, aluminum, and Mn to Mm (mesh metal) and the Ni alloy ($MmNi_5$:Mm=$La_{55}Ce_{30}Pr_3Nd_{12}$) which made the lantern the subject by arc melting. And machinery grinding of this was carried out at powder with a pitch diameter of about 100 micrometers using the ball mill, and hydrogen storing metal alloy powder ($MmNi_{3.5}Co_{0.7}$aluminum$_{0.3}Mn_{0.5}$ powder) was obtained. To hydrogen storing metal alloy powder and this hydrogen storing metal alloy powder, next, 0.5% of the weight of nickel powder, To this hydrogen storing metal alloy powder, respectively 0.1 % of the weight, 0.5 % of the weight, 1.0 % of the weight, 2.0 % of the weight, 3.0 % of the weight, 4.0 % of the weight, and 5.0% of the weight of calcium carbonate ($CaCO_3$) powder, The binder which consists of a mixture of 1.0% of the weight of an ethylene-vinylacetate copolymer and methyl cellulose to this hydrogen storing metal alloy powder was kneaded, and two or more pastes of viscosity 20,000 mPa-s were made. Next, after plastering with each paste both sides of the charge collector which consists of a punching metal about 0.1 mm thick with the doctor blade method, the hydrogen storing metal alloy electrode which performs desiccation and a press and constitutes a hydrogen storing metal alloy polar plate about 0.35 mm thick was obtained. Calcium carbonate powder was not added but others also obtained the hydrogen storing metal

alloy polar plate of the comparative example by the same method as the above.

[0008]Next, in order to investigate the characteristic of each polar plate, the alkaline battery which consists of a sealed type nickel hydrogen storage battery was made. The anode board was made as follows first. Nickel hydroxide powder and the binder which consists of 0.45% of the weight of carboxymethyl cellulose to this nickel hydroxide powder were kneaded first, and the paste was made. Next, after filling up with this paste the charge collector which consists of foaming nickel, desiccation, press, and decision were performed and the anode board of capacity 1300mAh was made. Next, each negative electrode plate (hydrogen storing metal alloy polar plate) was wound with the anode board via the separator which consists of a nonwoven fabric made of nylon, respectively, and the group of electrode was made. Next, after inserting each group of electrode in a cylindrical shape battery container, the electrolysis solution which becomes a group of electrode from the potassium hydroxide solution of 31 % of the weight of concentration was poured in, and the sealed type nickel hydrogen storage battery of anode capacity regulation of nominal capacity 1300mAh was made. And at the cell ambient air temperature of 20 **, it charged with the current of 0.1CmA for 16 hours, and the charge and discharge discharged until cell voltage is set to 1.0V with the current of 0.2CmA were repeated several times after performing publicly known activation to each cell. Occlusion of the hydrogen is carried out to a hydrogen storing metal alloy polar plate by this charge. And the experiments 1 and 2 were conducted next.

[0009](Experiment 1) At the cell ambient air temperature of 20 **, overdischarge of each cell was carried out until it was set to -1.0V with the current of 0.2CmA. And it discharged after charging with the current of 0.1CmA after overdischarge for 16 hours until it was set to 1.0V with the current of 0.2CmA. This investigated the relation of the amount of calcium carbonate and recovery capacity rate of the service capacity after the overdischarge to the service capacity before overdischarge of as opposed to [ask comparatively (recovery capacity rate) and] hydrogen storing metal alloy powder. Table 1 shows the measurement result.

[0010]

[Table 1]

炭酸カルシウム量 (重量%)	回復容量割合 (%)	-10℃/20℃の放電容量比 (%)
0	72	100
0.1	93	99
0.5	95	98
1.0	98	97
2.0	98	95
3.0	98	94
4.0	98	76
5.0	98	66

When a recovery capacity rate becomes large only by calcium carbonate being contained slightly and it is contained from this table 0.1% of the weight or more to hydrogen storing metal alloy powder, it turns out that a recovery capacity rate becomes almost fixed.

[0011](Experiment 2) In this experiment, the relation between the amount of calcium carbonate to hydrogen storing metal alloy powder and the temperature characteristics in the low temperature of a cell was investigated. First, in cell ambient-air-temperature-10 **, it discharged after charging each cell with the current of 0.1CmA for 16 hours until it was set to 1.0V with the current of 0.2CmA, and service capacity was measured. Also at the cell ambient air temperature of 20 **, it discharged after charging each cell with the current of 0.1CmA for 16 hours until it was set to 1.0V with the current of 0.2CmA, and service capacity was measured. And the service capacity at -10 ** to the service capacity at 20 ** computed comparatively (service capacity ratio of -10 **/20 **), and the relation with the service capacity ratio of the amount of calcium carbonate, -10 **/20 ** to hydrogen storing metal alloy powder was investigated. The measurement result is shown in Table 1.

[0012]When the amount of calcium carbonate to hydrogen storing metal alloy powder exceeds 3.0 % of the weight from this table, it turns out that the service capacity ratio of -10 **/20 ** falls, and a battery characteristic falls.

[0013]As mentioned above, a thing with preferred considering it as 0.1 to 3.0 % of the weight to a hydrogen storing metal alloy understands the content of calcium carbonate from the experiments 1 and 2.

[0014]

[Effect of the Invention]Even if calcium carbonate will perform overdischarge like this invention if it makes an active material layer contain calcium carbonate since it has the operation which raises oxygen overpotential, it can control generating of oxygen gas. Therefore, oxidation of a hydrogen storing metal alloy can be controlled and the fall of the hydrogen absorption characteristic of a hydrogen storing metal alloy can be controlled. As a result, service capacity is recoverable even if it carries out overdischarge of the cell.

[Translation done.]